(12) **EUROPEAN PATENT SPECIFICATION**

(54) **BANDGAP TUNING OF SEMICONDUCTOR WELL STRUCTURE**

ABSTIMMEN DES BANDABSTANDS EINER HALBLEITENDEN QUANTUMWELL-STRUKTUR

ACCORD PAR BANDE INTERDITE DE LA STRUCTURE A PUITS DE SEMI-CONDUCTEUR

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Description

[0001] This invention relates to semiconductor heterostructures and, more specifically, to a method of bandgap tuning a quantum well structure in a spatially selective manner.

[0002] The invention can also be applied to post processing to modify device properties. The invention provides a useful and new method for the monolithic integration of multi-use devices on a single substrate with simplified growth topology.

[0003] Optical and electrical properties of quantum well structures are of great importance for novel semiconductor device applications. The ultimate goal of monolithic integration of optical, optoelectronic and electronic components requires the capability for controllable lateral and vertical modifications of optical constants and electrical characteristics in such components.

[0004] Present techniques include etching and regrowth. Regrowth involves growing a device structure such as a laser, and then etching away the regions where other components, such as modulators etc., are desired and regrowing these components. This involves a large number of processing steps, with problems associated with growing good quality material after etching, leading to poor device yields.

[0005] US patent no. 5,238,868 describes in detail a technique for shifting the bandgap using quantum well intermixing. This technique involves mixing quantum well material with surrounding barrier material to change the bandgap of the quantum well. This is performed by introducing impurities or defects into the quantum well in the region of the wafer that requires a modification of the bandgap. The implanted wafer is then annealed to intermix the defects and shift the bandgap. This technique does not, however, permit different regions of the wafer to be selectively tuned.

[0006] An object of the invention is to alleviate these problems.

[0007] According to the present invention there is provided a a method of bandgap tuning a quantum well heterostructure wherein ions are implanted into the heterostructure to create defects therein, and the heterostructure is then annealed to initiate intermixing in the quantum well region, characterized in that ions initially of a single energy are implanted in a single-ion implantation step into different regions in a spatially selective manner through a mask of varying height or varying density so that the different regions are implanted with ions of different energy to create different concentrations of defects in the different regions and thereby result in different bandgap shifts during subsequent annealing after removal of the mask.

[0008] Tuning the bandgap of a quantum well structure during subsequent thermal treatment in a spatially selective manner in this way is a powerful technique for performing monolithic integration. This allows the fabri-

cation of lasers (of many wavelengths), detectors, waveguides, modulators, etc. on a single wafer.

[0009] In one embodiment, the ions are implanted through a mask, for example of SiO_2, of varying thickness at a single energy, for example, of about 1 MeV. This varies the energy of ions reaching different regions, resulting in different concentrations of defects in the semiconductor. A thin SiO_2 layer will slow down the ions so that they will reach the surface of the semiconductor slower than they would in the absence of the mask, and hence will result in a smaller bandgap shift. A very thick mask will stop the ions completely and will result in no shift. Therefore, by varying the thickness of the mask, the degree of damage can be controlled. The mask may be removed prior to thermal treatment, although this is not necessary.

[0010] In another embodiment, the ions are implanted through a mask of varying density to achieve a similar result. In other embodiments, alternative techniques are employed to vary the dosage in a spatially selective manner.

[0011] The inventive technique works because of dependence of the shift in quantum well bandgap on defect concentration, which in turn is dependent on ion energy and/or dosage. The greater the dose, or the higher the energy of the implanted ions, the more damage that will be done. This invention provides the enabling technology for the integration and modification of optoelectronic components on a monolithic structure.

[0012] The invention will now be described in more detail, by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 shows the change in quantum well bandgap due to ion implantation into an unmasked structure at different ion energies for an InP based quantum well laser;

Figure 2(a) shows a typical photonic circuit that has been created using this technique;

Figure 2(b) shows a SiO_2 masking pattern that is used in a method according to the invention and the resulting different shifts in bandgap caused by ions of different energies;

Figure 3 shows a precursor of an extended spectrum super luminescent diode (SLD) and the output spectrum of the resulting;

Figure 4 is a schematic diagram of two sections of a demultiplexer fabricated in accordance with the invention;

Figure 5 shows the wavelength response of the two photodetectors in the demultiplexer;

Figure 6 shows an example useful for the understanding of the invention using focused ion implantation;

Figure 7 shows an embodiment employing a multiple thickness mask; and

Figure 8a shows a further embodiment employing a multiple thickness contact mask;

Figure 8b shows an embodiment employing a multiple thickness contact mask created using a shadow masking technique;

Figure 9a shows an example useful for the understanding of the invention with multiple ion implants using contact masks; and

Figure 9b shows an example useful for the understanding of the invention with multiple ion implants using shadow masks.

[0013] Figure 1 shows the change in quantum well bandgap with ion implantation energy for an InP based quantum well laser. This has been implanted with different energy P ions at a dose of 2.5×10^{13} cm^{-2}, and then annealed at 700°C for 60 seconds. As can be seen from Figure 1, there is a strong dependence of bandgap shift on ion energy up to 2 MeV. By implanting, for example, 2 MeV ions through a SiO$_2$ mask using standard technology compatible with InP processing, any bandgap shift from 0 to 41 meV can be obtained with a single ion implant. This can be performed purely by varying the mask thickness, although other means to vary the implanted dose can be employed.

[0014] Figure 2(a) shows a typical photonic circuit that can be created using the above technique. It consists of a laser 1, a modulator 2, which controls the output of the laser 1, and a waveguide 3 to send the light to another region of the wafer 4, or an optical fiber.

[0015] By using an SiO$_2$ mask 5 of varying thickness, as shown in Figure 2(b), different defect concentrations are created in different regions of the wafer using a single ion implantation step. As ions travel through the SiO2 they are slowed down, i.e. they decrease in energy. The thicker the SiO2, the more the ions are slowed, until they are stopped completely. The mask is implanted with ions of a single energy, e.g. 1 MeV, but the surface of the wafer actually receives ions with different energies, 0 to 1MeV, depending on the thickness of the SiO$_2$ that the ions travel through. The resulting wafer is annealed, causing different shifts in bandgap for the different regions. The result is a bandgap profile suitable for the fabrication of a photonic integrated circuit.

[0016] Using this process, a standard quantum well laser wafer can be processed into any photonic integrated circuit simply by changing the SiO$_2$ mask used for implantation. For example, the wafer used to create the device shown in Figure 2(a) could easily have been used to make a sensor for detecting a specified chemical compound. A tuned laser/detector pair would be made with an air gap between them. The presence of the specified chemical in the air gap would lead to an absorption of the laser light, and a drop in the signal from the detector.

[0017] New devices can also be implemented, such as an extended-gain-spectrum laser or an extended spectrum super luminescent diode (SLD) shown in Figure 3. Normally, the output spectrum of an SLD is directly limited to the gain spectrum, which is typically 20-30 nm. There are numerous applications, such as fiber based gyroscopes and broad band illumination sources for spectroscopy, for SLDs with an output spectrum approaching 100 nm or greater. To extend the output spectrum of this device, a variable thickness mask is used along the length of the laser cavity (Figure 3a). After ion implantation, the gain spectrum is shifted in wavelength by different amounts in different sections of the cavity (Figure 3b). This results in a total gain spectrum, the dashed line, which is almost flat, and covers a wider frequency range than the untreated material.

[0018] The addition of a high reflecting coating on the Facet 1 (Figure 3(a)) and anti-reflection coating on Facet 2 (Figure 3(a)) results in a uni-directional extended spectrum SLD. Mirrors on both facets result in an extended-gain-spectrum laser. With anti-reflection coatings on both facets, an amplifier can be made with an extended wavelength gain.

[0019] In a further embodiment, instead of varying the thickness of the mask, it is possible to vary the density. This can be achieved, for example, by depositing an SiO$_2$ mask on some regions of the surface of the heterostructure and then sputtering metal on other regions where it is desired to have a higher density mask.

[0020] In Figure 4, a monolithic demultiplexer comprises a substrate 30 and an InP based laser structure 31. Photodetectors 32, 33 are formed over different regions of the structure, which has been subjected to bandgap tuning in accordance with the invention. In the structure of Figure 4, four different thicknesses (0, 0.65, 1.2 and 2.2µm) of SiO$_2$ mask were evaporated onto the sample surface. Phosphorus ions were implanted into the sample through the mask at a dose of 2.5×10^{13} cm^{-2} with an energy of 1MeV. The thickest SiO2 region was designed to stop the 1 MeV ions completely. During implantation the sample was tilted at and angle of 7°C to the surface normal to minimize ion channeling.

[0021] After ion implantation the mask was removed. This was followed by an anneal at 700°C for 90 seconds in a nitrogen atmosphere, using a Heatpulse 410 Rapid Thermal Annealer. During the annealing, the defects diffused rapidly through the InP material and the quantum well (QW) region causing an intermixing of the QW and barrier layers. This resulted in a shift of the QW absorption edge that was greatest for the region which had had no SiO$_2$ mask above it, and decreased as the SiO$_2$ mask layers increased in thickness. The region under the thickest SiO$_2$ layer had no shift in the QW absorption edge at all.

[0022] Separate gold contact pads were put on each of the differently masked regions to create a photodetector array. Light was coupled into the structure passing from the strongly intermixed into the non-intermixed region. Since the QW bandgap in each of the masked regions was different, the wavelength response for each was modified.

[0023] As can be seen in Figure 5, the response of photodetector 1, which lies over the bandgap shifted re-

gion, is shifted about 80 nm to the left.

[0024] This simple device allows the demultiplexing of a wavelength division multiplexed signal.

[0025] In an example useful for the understanding of the invention an alternative method of manufacture, shown in Figure 6, regions having different concentrations of defects are created by using a scanning microbeam or projection ion beam system. A suitable practical example is a focused ion beam (FIB) machine. By varying the ion beam current, or by repetitive patterning, the number of defects can be adjusted in a lateral manner on the wafer. In step 1, the left side of the wafer is subjected to a large ion dose, and in step 2, the right side is subjected to a small ion dose.

[0026] After a repetitive scan in step 3, the wafer is subjected to a single rapid thermal anneal (RTA) in step 4 to effect a bandgap shift that depends on the concentration of defects, and thus the ion dose in the various regions. The Quantum well bandgap shifts reflect the defect density produced by the complex ion implantation pattern written on the wafer.

[0027] Figure 7 shows in detail a method of making a wafer employing a single, multiple thickness mask. After despositing an SiO_2 layer 11 on wafer surface 1 (step 1), a temporary mask 12 is applied to cover a portion of the wafer surface, and a deep etch (step 3) is performed on the remainder. The temporary mask 12 is removed and a second SiO_2 deposition 13 performed. The process is repeated through steps 6 to 12 adding additional SiO2 layers 15 and employing masks 14, 16 to produce a multiple thickness mask as shown at step 12. Finally, in step 13, the wafer is subjected to ion implantation. Clearly, the exposed region receives the greatest ion dose and thus exhibits the greatest band gap shift.

[0028] Figure 8a shows the use of a single multiple thickness contact mask. As in Figure 7, an SiO2 mask 11 is formed on the surface of the wafer 10. A temporary mask 12 applied to cover parts of the exposed surface. A deep etch (step 3) is then performed and the temporary mask 12 removed. A second temporary mask 14 is applied and a shallow etch performed, which after removal of the mask 14, produces the stepped structure shown in step 7.

[0029] An ion implantation is then performed as shown in step 8. The thicker the mask the lower the ion energy reaching the sample surface, and hence the lower the concentration of defects. Thus, after intermixing the region with no mask exhibits the largest bandgap shift, and the region under the thickest portion of the mask, which does not receive any ions, exhibits no shift at all.

[0030] Figure 8b shows how a similar result can be achieved using a shadow mask 20. The stepped mask 11, 21 is built up in a series of steps where the region over which it is not desired to deposit an SiO_2 layer is covered with shadow mask 20. In step 5, a single implant and anneal is performed to create different densities of defects and thus different bandgap shifts.

[0031] Figure 9a shows in an example useful for the understanding of the invention how a variable density defect concentration can be achieved using multiple implants with a single mask.

[0032] An ion implantation is performed through a first temporary mask 12 into the wafer 10. A second mask 14 is then applied over different regions and a second implantation carried out in step 5. The regions that are exposed more than once receive a greater dose of ions and thus have a greater defect concentration. After annealing, these have the greatest bandgap.

[0033] Figure 9b shows in an example useful for the understanding of the invention a similar case for a shadow mask 20. Clearly, the exposed region receives the ions with the greatest energy and thus exhibits the greatest bandgap shift. The dose delivered by each implantation step differs, resulting in a wafer in which different areas experience different defect concentrations and thus shift differently during anneal. The anneal can be a single anneal, after all the doses have been applied, or separate anneals after each dose.

[0034] The described technique allows the monolithic integration of multi-use devices on a single substrate without deterioration of the material quality after the process.

Claims

1. A method of bandgap tuning a quantum well heterostructure (1;10;31) wherein ions are implanted into the heterostructure (1;10;31) to create defects therein, and the heterostructure is then annealed to initiate intermixing in the quantum well region, characterized in that ions initially of a single energy are implanted in a single-ion implantation step into different regions in a spatially selective manner through a mask (5;11,13,15) of varying height or varying density so that the different regions are implanted with ions of different energy to create different concentrations of defects in the different regions and thereby result in different bandgap shifts during subsequent annealing after removal of the mask (5; 11,13,15).

2. A method as claimed in any one of claim 1, characterized in that the mask (5;11,13,15) is an SiO_2 mask.

3. A method as claimed in any one of claims 1 and 2, characterized in that the ions initially have a single energy of about 1 MeV.

4. A method as claimed in any one of claims 1 to 3, characterized in that the heterostructure is an InP-based quantum well laser (1;10;31)

5. A method as claimed in any one of claims 1 to 3,

characterized in that the heterostructure is a super-luminescent diode.

6. A method as claimed in any one of claims 1 to 3, characterized in that the heterostructure is a demultiplexer for wavelength division multiplexing.

7. A method as claimed in any one of claims 1 to 3, characterized in that the heterostructure is an integrated internal laser modulator.

8. A method as claimed in any one of claims 1 to 3, characterized in that the heterostructure is a single mode waveguide laser.

9. A method as claimed in any one of claims 1 to 3, characterized in that the heterostructure is a transparent facet for a high-powered laser.

10. A method as claimed in claim 1, characterized in that the heterostructure (1;10;31) is annealed at about 700° for about 60 seconds.

11. A method as claimed in claim 1, characterized in that said mask (5) of varying height is formed by successively depositing overlapping mask layers (11,13,15) covering different regions onto the heterostructure (1;10;31).

12. A method as claimed in claim 11, characterized in that said mask (5) of varying height is formed by sequentially depositing a first mask layer (11) on said heterostructure (10), depositing a first temporary mask layer (12) over a portion of said first mask layer (11), etching an exposed portion of said first mask layer (11), removing said first temporary mask layer (12), depositing a second mask layer (13) on said first mask layer (11), depositing a second temporary mask layer (14) over a portion of said second mask layer (13), and so on to build up a composite multilayer mask of varying height.

Patentansprüche

1. Verfahren zur Bandlückenabstimmung einer Quantentopf-Heterostruktur (1; 10; 31), wobei Ionen in die Heterostruktur (1; 10; 31) zur Erzeugung von Defekten darin implantiert werden und die Heterostruktur dann getempert wird, um eine Vermischung in dem Quantentopfbereich zu initiieren, dadurch gekennzeichnet, daß anfänglich Ionen einer einzelnen Energie in einem Einzelionen-Implantationsschritt in verschiedene Bereiche in einer räumlich selektiven Art und Weise durch eine Maske (5; 11, 13, 15) variierender Höhe oder variierender Dichte implantiert werden, so daß die verschiedenen Bereiche mit Ionen verschiedener Energie implantiert

werden, um verschiedene Konzentrationen von Defekten in den verschiedenen Bereichen zu erzeugen und dadurch in verschiedenen Bandlückenverschiebungen während des darauffolgenden Temperns nach Entfernen der Maske (5; 11, 13, 15) zu resultieren.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Maske (5; 11, 13, 15) eine SiO_2-Maske ist.

3. Verfahren nach einem der Ansprüche 1 und 2, dadurch gekennzeichnet, daß die Ionen anfänglich eine einzelne Energie von etwa 1 MeV aufweisen.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Heterostruktur ein InP-basierter Quantentopflaser (1; 10; 31) ist.

5. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Heterostruktur eine superlumineszente Diode ist.

6. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Heterostruktur ein Demultiplexierer zur Wellenlängenteilungs-Multiplexierung ist.

7. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Heterostruktur ein integrierter innerer Lasermodulator ist.

8. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Heterostruktur ein Einzelmodem-Wellenleiterlaser ist.

9. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Heterostruktur eine transparente Facette für einen Hochleistungslaser ist.

10. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Heterostruktur (1; 10; 31) bei etwa 700° für etwa 60 Sekunden getempert wird.

11. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Maske (5) variierender Höhe durch sukzessives Abscheiden überlappender Maskierungsschichten (11, 13, 15), welche verschiedene Bereiche auf der Heterostruktur (1; 10; 31) bedecken, gebildet wird.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß die Maske (5) variierender Höhe durch sequentielles Abscheiden einer ersten Maskierungsschicht (11) auf der Heterostruktur (10), Abscheiden einer ersten temporären Maskierungsschicht (12) über einem Abschnitt der ersten Mas-

kierungsschicht (11), Ätzen eines freigelegten Ab-
schnitts der ersten Maskierungsschicht (11), Entfer-
nen der ersten temporären Maskierungsschicht
(12), Abscheiden einer zweiten Maskierungs-
schicht (13) auf der ersten Maskierungsschicht (11),
Abscheiden einer zweiten temporären Maskie-
rungsschicht (14) über einen Abschnitt der zweiten
Maskierungsschicht (13) und so weiter zum Auf-
bauen einer zusammengesetzten mehrschichtigen
Maske variierender Höhe gebildet wird.

Revendications

1. Procédé d'accord en bande interdite d'une hétéros-
tructure à puits quantique (1; 10; 31) dans lequel
des ions sont implantés dans l'hétérostructure (1;
10; 31) afin de créer des défauts dedans, et l'hété-
rostructure est ensuite soumise à un recuit afin d'ini-
tier un intermélange dans la région de puits quanti-
que, caractérisé en ce que des ions initialement
d'une unique énergie sont implantés lors d'une éta-
pe d'implantation d'ions uniques dans des régions
différentes d'une façon sélective spatialement au
travers d'un masque (5; 11, 13, 15) de hauteur va-
riable ou de densité variable de telle sorte que les
régions différentes soient implantées à l'aide d'ions
d'énergies différentes afin de créer des concentra-
tions différentes de défauts dans les régions diffé-
rentes et d'ainsi aboutir à des décalages de bande
interdite différents pendant un recuit ultérieur après
enlèvement du masque (5; 11, 13, 15).

2. Procédé selon la revendication 1, caractérisé en ce
que le masque (5; 11, 13, 15) est un masque en
SiO_2.

3. Procédé selon l'une quelconque des revendications
1 et 2, caractérisé en ce que les ions présentent
initialement une unique énergie d'environ 1 MeV.

4. Procédé selon l'une quelconque des revendications
1 à 3, caractérisé en ce que l'hétérostructure est un
laser à puits quantique à base de InP (1; 10; 31).

5. Procédé selon l'une quelconque des revendications
1 à 3, caractérisé en ce que l'hétérostructure est
une diode superluminescente.

6. Procédé selon l'une quelconque des revendications
1 à 3, caractérisé en ce que l'hétérostructure est un
démultiplexeur pour un multiplexage par division en
longueur d'onde.

7. Procédé selon l'une quelconque des revendications
1 à 3, caractérisé en ce que l'hétérostructure est un
modulateur à laser interne intégré.

8. Procédé selon l'une quelconque des revendications
1 à 3, caractérisé en ce que l'hétérostructure est un
laser à guide d'ondes monomode.

9. Procédé selon l'une quelconque des revendications
1 à 3, caractérisé en ce que l'hétérostructure est
une facette transparente pour un laser haute puis-
sance.

10. Procédé selon la revendication 1, caractérisé en ce
que l'hétérostructure (1; 10; 31) est soumise à un
recuit à environ 700° pendant environ 60 secondes.

11. Procédé selon la revendication 1, caractérisé en ce
que ledit masque (5) de hauteur variable est formé
en déposant successivement des couches de mas-
que en chevauchement (11, 13, 15) qui recouvrent
des régions différentes sur l'hétérostructure (1; 10;
31).

12. Procédé selon la revendication 11, caractérisé en
ce que ledit masque (5) de hauteur variable est for-
mé en déposant séquentiellement une première
couche de masque (11) sur ladite hétérostructure
(10), en déposant une première couche de masque
temporaire (12) au-dessus d'une partie de ladite
première couche de masque (11), en gravant une
partie mise à nu de ladite première couche de mas-
que (11), en enlevant ladite première couche de
masque temporaire (12), en déposant une seconde
couche de masque (13) sur ladite première couche
de masque (11), en déposant une seconde couche
de masque temporaire (14) au-dessus d'une partie
de ladite seconde couche de masque (13) etc...
pour ainsi constituer un masque multicouche com-
posite de hauteur variable.

FIG. 1

1 2 4 3

FIG. 2a

Single ion implantation at one energy

5

SiO$_2$ mask

4

} Laser structure

Laser bandgap   Modulator bandgap   Waveguide bandgap

Absorption

Energy   **FIG. 2b**

Single ion implantation at one energy
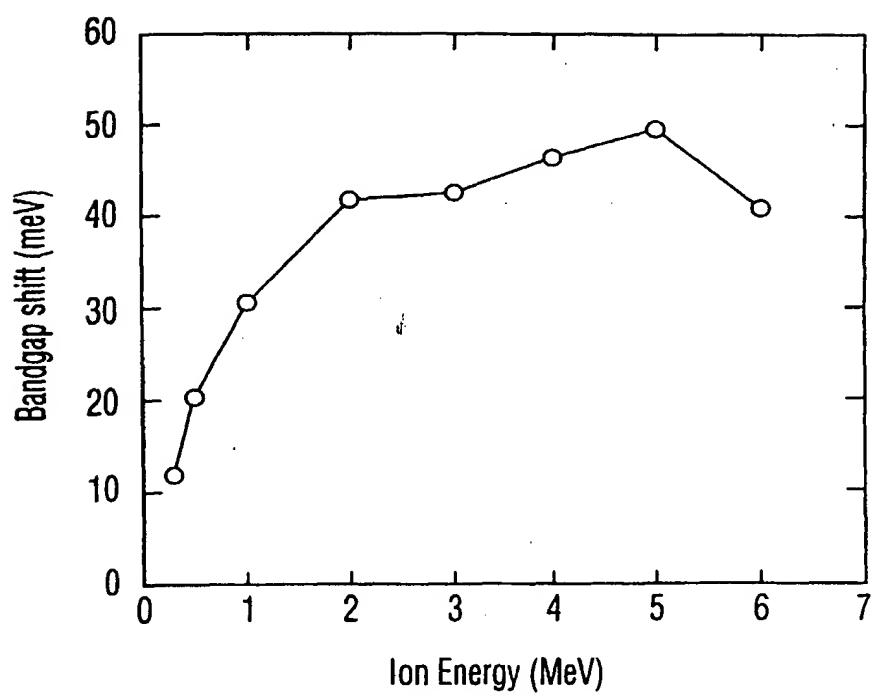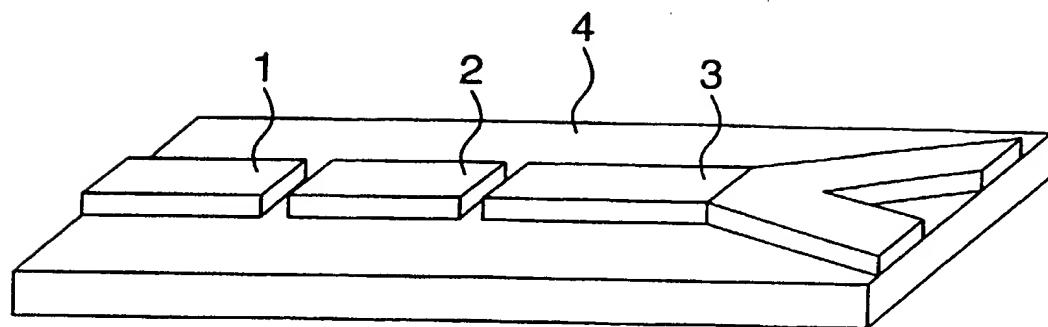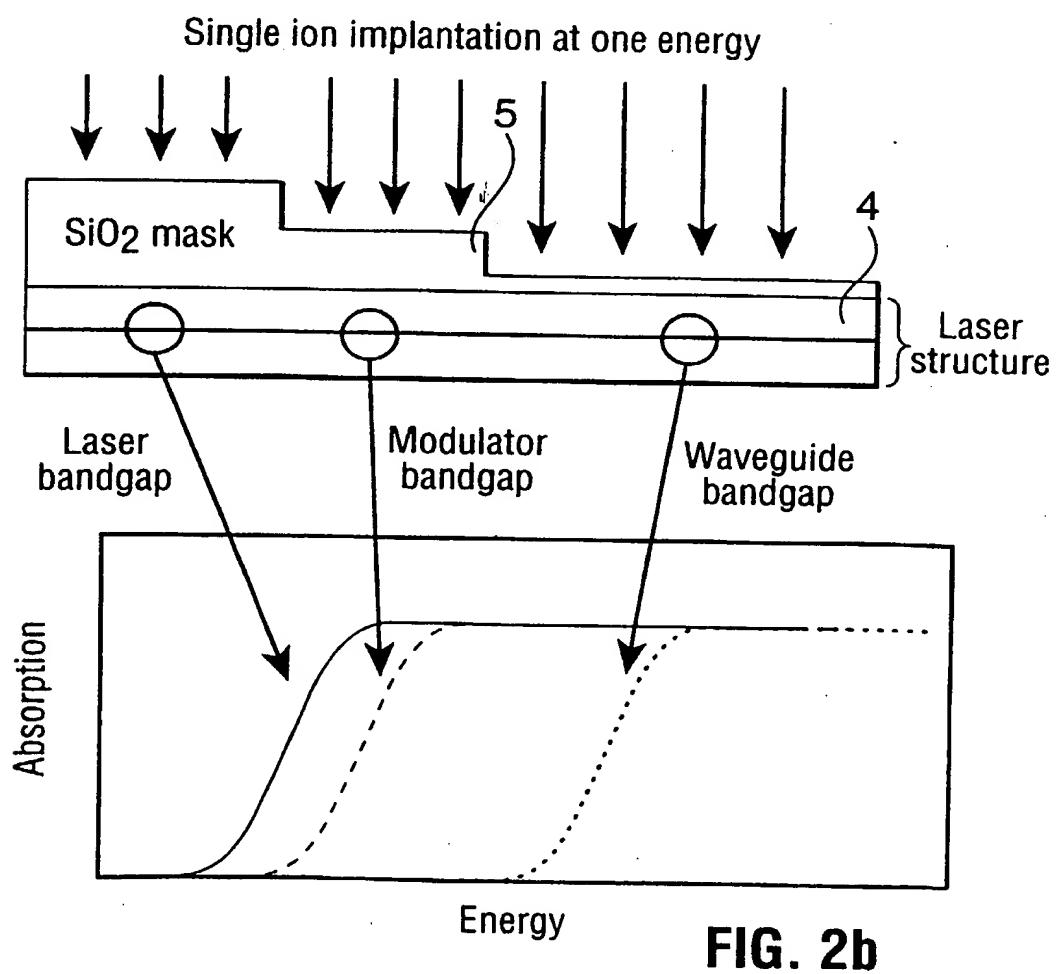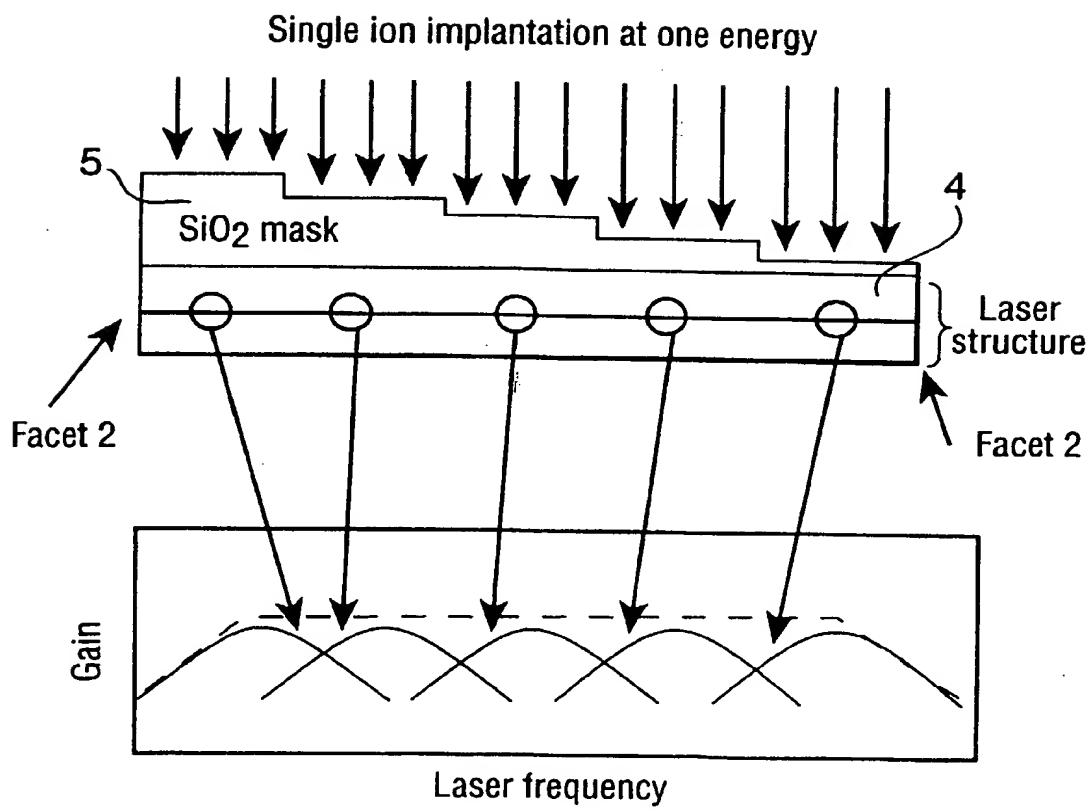
FIG. 3
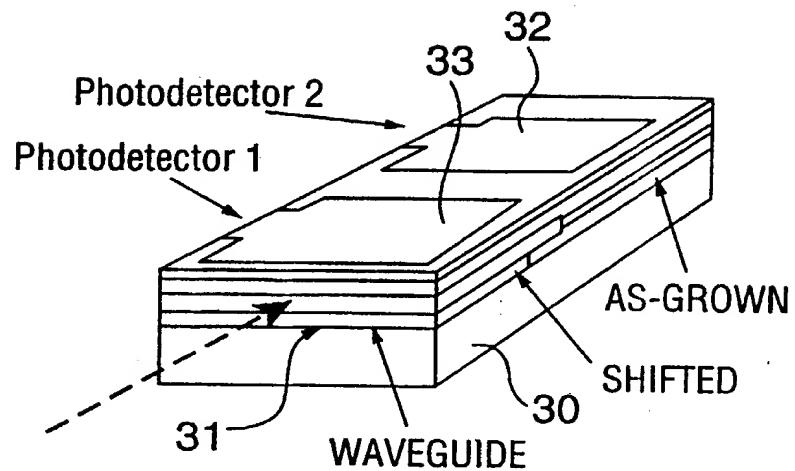
FIG. 4
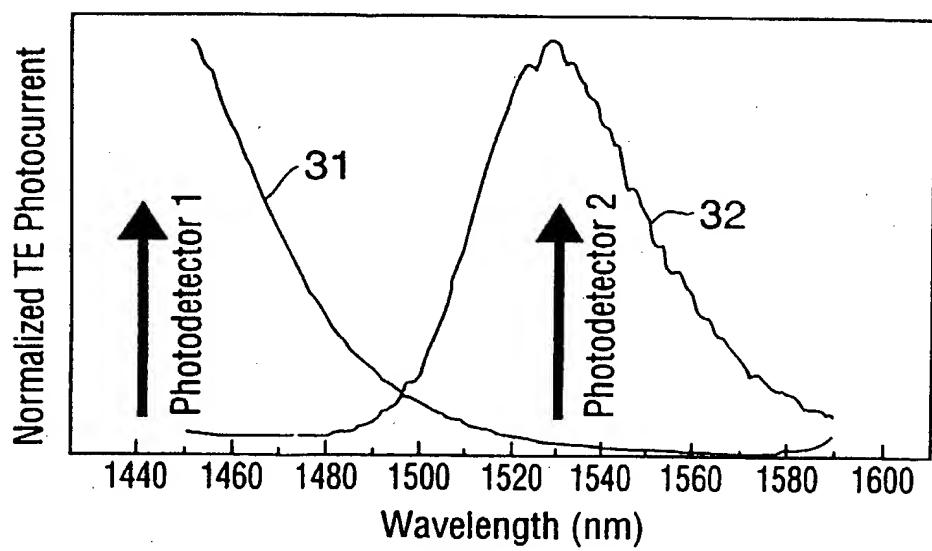
FIG. 5

Scanning Ion Beam Implantation

1) large ion dose

2) small ion dose

3) repetitive scan

4) perform single anneal

medium shift

large shift

small shift

no shift
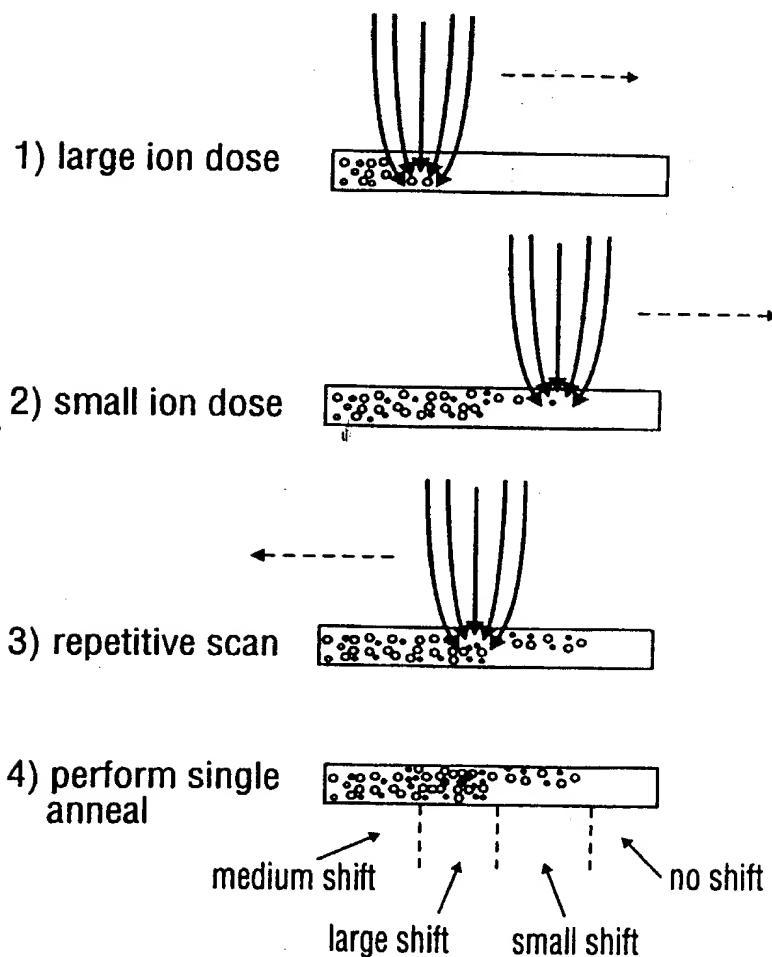
FIG. 6

Multiple Thickness Mask [Contact Mask]

1) deposit SiO₂ — 11, 10

2) temp mask 1 — 12, 11, 10

3) etch — 12, 11, 10

4) remove mask — 11, 10

5) second deposition — 13, 11, 10

6) temp mask 2 — 14, 13, 11, 10

7) etch — 14, 13, 11, 10

8) remove mask — 13, 11, 10

9) third deposition — 15, 13, 11, 10

10) temp mask 3 — 16, 15, 13, 11, 10

11) etch — 16, 15, 13, 11, 10

12) remove mask — 15, 13, 11, 10

13) perform single implant and anneal step — 15, 13, 11, 10

medium shift   large shift   small shift   no shift
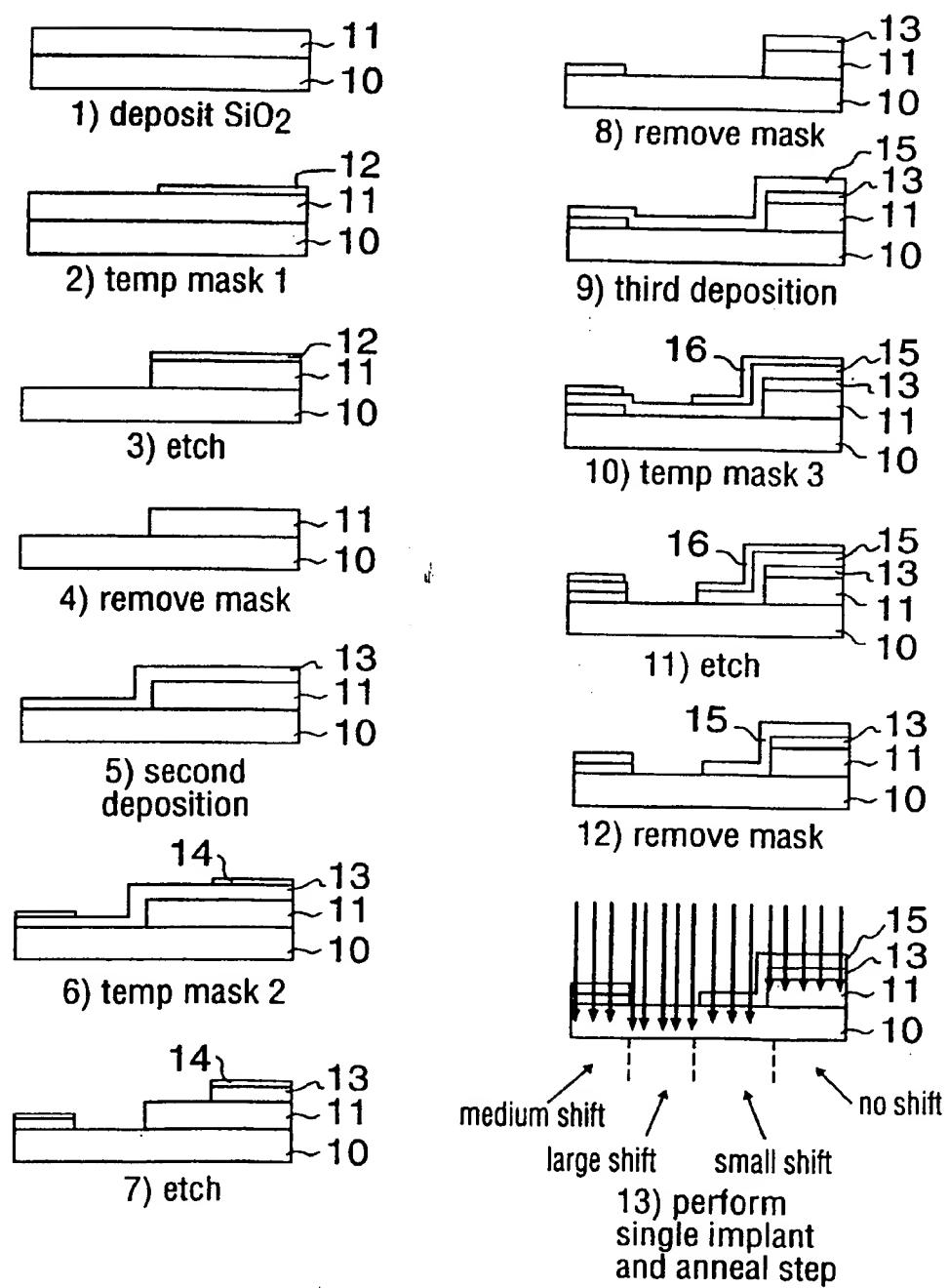
FIG. 7

Multiple Thickness Mask
(a) Contact Masks

1) SiO$_2$
  — 11
  — 10

2) temp mask 1
  — 12
  — 11
  — 10

3) deep etch
  — 12
  — 11
  — 10

4) remove mask
  — 11
  — 10

5) temp mask 2
  — 14
  — 11
  — 10

6) shallow mask
  — 14
  — 11
  — 10

7) remove mask
  — 11
  — 10

8) perform single implant and anneal

10 —

medium shift   large shift   small shift   no shift
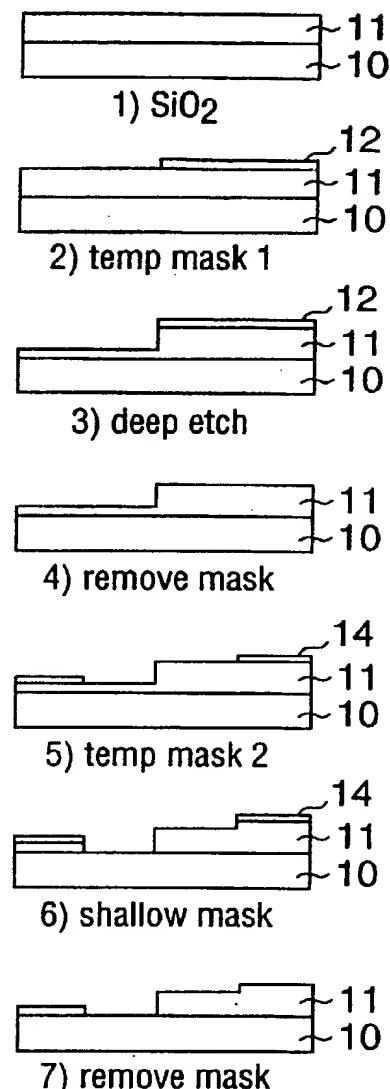
FIG. 8a

Multiple Thickness Mask
(b) Contact Masks

1) shadow mask 1
  20 —
  — 10

2) thick layer
  11 —
  20
  — 10

3) shadow mask 2
  20 —
  11 —
  20
  — 10

4) thin layer
  20 —   21
  11 —   20
  — 10

5) perform single implant and anneal

21
11 —
10 —

medium shift   large shift   small shift   no shift

**FIG. 8b**

Multiple Implants
(a) Contact Masks

Multiple Implants
(a) Contact Masks

1) mask 1

1) mask 1

2) large ion dose

2) large ion dose

3) remove mask

3) mask 2

4) mask 2

4) small ion dose

5) small ion dose

5) perform single anneal

medium shift

large shift   small shift   no shift

FIG. 9b

medium shift   no shift

large shift   small shift

6) remove mask
and perform
single annneal

FIG. 9a